



(11) **EP 1 221 493 A1**

(12)

- (87) International publication number:  
WO 01/86013 (15.11.2001 Gazette 2001/46)

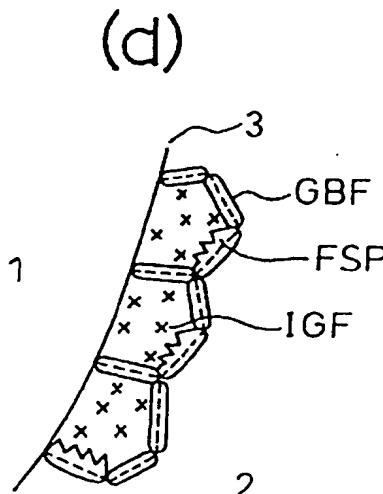
- (72) Inventors:
- KOJIMA, Akihiko,  
Nippon Steel Corp. Kimitsu Works  
Kimitsu-shi, Chiba 299-1193 (JP)
  - TERADA, Yoshio,  
Nippon Steel Corp. Kimitsu Works  
Kimitsu-shi, Chiba 299-1193 (JP)

- KIYOSE, Akihito,  
Nippon Steel Corp. Techn. Devel.  
Futtsu-shi, Chiba (JP)
- YOSHIDA, Yuzuru,  
Nippon Steel Corp. Kimitsu Works  
Kimitsu-shi, Chiba 299-1193 (JP)
- ADACHI, Toshihiko, Nippon Steel Corporation  
Chiyoda-ku, Tokyo 100-8071 (JP)
- TANAKA, Kazuaki,  
Nippon Steel Corp. Kimitsu Works  
Kimitsu-shi, Chiba 299-1193 (JP)
- UEMORI, Ryuji,  
Nippon Steel Corp. Techn. Devel.  
Futtsu-shi (JP)
- IMAI, Shiro, Nippon Steel Corporation  
Chiyoda-ku, Tokyo 100-8071 (JP)

- (74) Representative: **VOSSIUS & PARTNER**  
**Siebertstrasse 4**  
**81675 München (DE)**

- (54) **THICK STEEL PLATE BEING EXCELLENT IN CTOD CHARACTERISTIC IN WELDING HEAT AFFECTED ZONE AND HAVING YIELD STRENGTH OF 460 Mpa OR MORE**

(57) The object of the present invention is to provide a steel plate having a yield strength not lower than 460 MPa and CTOD in a HAZ not less than 0.2 mm at -10°C. The present invention is a steel plate having an excellent CTOD property in a weld heat-affected zone and a yield strength not lower than 460 Mpa, characterized by: having a chemical composition comprising, in terms of wt%, C: 0.04 to 0.14 %, Si: 0.4 % or less, Mn: 1.0 to 2.0 %, P: 0.02 % or less, S: 0.001 to 0.005 %, Al: 0.001 to 0.01 %, Ti: 0.005 to 0.03 %, Nb: 0.005 to 0.05 %, Mg: 0.0003 to 0.005 %, O: 0.001 to 0.005 %, and N: 0.001 to 0.01 %; with the balance consisting of iron and unavoidable impurities: and having TiN particles of 0.01 to 0.5  $\mu\text{m}$  at not less than 10,000 pieces/ $\text{mm}^2$  containing oxide composed of Mg and Al, and particles of 0.5 to 10  $\mu\text{m}$  at not less than 10 pieces/ $\text{mm}^2$  containing not less than 0.3 wt% of Mn in the compounded form of oxide and sulfide.



## Description

### Technical Field

**[0001]** The present invention relates to a steel plate having an excellent CTOD (Crack Tip Opening Displacement) property in a weld heat-affected zone (HAZ) and a yield strength not lower than 460 MPa, preferably in the class of 500 to 550 MPa, mainly used for offshore structures, and also applicable to other welded structures of which strengths and HAZ toughness (CTOD property) on a comparable level are required.

### Background Art

**[0002]** A CTOD property at -10°C is required of welded joints in-offshore structures used in the Northern Sea. As a steel product of which such strict HAZ toughness is required, Ti-oxide steel is used as is described, for example, in "Proceedings of 12th International Conference on OMAE, 1993, Glasgow, UK, ASME, Volume III-A, pp.207 - 214." Because portions of a HAZ in close proximity to a fusion line are heated to 1,400°C or higher, a pinning effect by TiN particles becomes lost, austenite ( $\gamma$ ) grains are markedly coarsened, and also the structure of the HAZ is coarsened, thus deteriorating the toughness thereof. The Ti-oxide steel described above has been developed as a steel that solves such a problem.

**[0003]** This technology provides a steel in which a HAZ structure is fined by using acicular ferrite grains that are generated with thermally stable Ti oxide particles used as transformation nuclei in  $\gamma$  grains coarsened due to the loss of the pinning effect of TiN particles, as is described in Japanese Unexamined Patent Publication Nos. S63-210235 and H6-075599, for example. The acicular ferrite grains which effectively fine coarse  $\gamma$  grains are called intragranular transformed ferrite (IGF) grains.

**[0004]** However, the yield strength of this Ti-oxide steel is not higher than 420 MPa, and no steel plate has been developed that assures a CTOD property in its HAZ while having a yield strength higher than 420 MPa. Meantime, there is a strong requirement to reduce the construction cost of offshore structures by reducing the weight, and therefore a steel plate having a higher yield strength is required in order to reduce the weight of offshore structures. That is, a steel plate is strongly required which is able to assure a CTOD property while having a yield strength not lower than 460 MPa, a strength higher than any available.

### Disclosure of the Invention

**[0005]** The object of the present invention is to provide a steel plate having a yield strength not lower than 460 MPa, preferably in the class of 500 to 550 MPa, and a CTOD not less than 0.2 mm in a HAZ at -10°C.

**[0006]** The present invention is a steel plate having an excellent CTOD property in a weld heat-affected zone and a yield strength not lower than 460 Mpa, characterized by:

having a chemical composition; comprising, in terms of wt%,

C: 0.04 to 0.14 %,  
Si: 0.4 % or less,  
Mn: 1.0 to 2.0 %,  
P: 0.02 % or less,  
S: 0.001 to 0.005 %,  
Al: 0.001 to 0.01 %,   
Ti: 0.005 to 0.03 %,   
Nb: 0.005 to 0.05 %,   
Mg: 0.0003 to 0.005 %,   
O: 0.001 to 0.005 %, and   
N: 0.001 to 0.01 %;

further, when a need arises, comprising, in terms of wt%, one or more of

Ca: 0.0005 to 0.005 %,   
REM: 0.0005 to 0.01 %,   
Zr: 0.0005 to 0.01 %,   
Cu: 0.05 to 1.5 %,   
Ni: 0.05 to 3.0 %,   
Cr: 0.05 to 0.5 %,

Mo: 0.05 to 0.5 %,  
 V: 0.005 to 0.05 %, and  
 B: 0.0001 to 0.003 %,

wherein the total amount of Ca, REM, and Zr is not more than 0.02 % and the total amount of Cu, Ni, Cr, and Mo is not more than 3.0 %; with the balance consisting of iron and unavoidable impurities: and

having TiN particles of 0.01 to 0.5  $\mu\text{m}$ , at a rate of not less than 10,000 pieces/ $\text{mm}^2$ , containing oxides composed of Mg and Al, and particles of 0.5 to 10  $\mu\text{m}$  at a rate of not less than 10 pieces/ $\text{mm}^2$ , containing not less than 0.3 wt% of Mn in the compounded form of oxide and sulfide.

#### Brief Description of the Drawings

#### [0007]

Figs. 1 (a) to (d) are illustrations schematically showing the concept of HAZ structure control for a steel plate having an excellent CTOD property in its weld heat-affected zone and a yield strength not lower than 460 MPa according to the present invention. Fig. 1 (a) illustrates a HAZ structure in a conventional Ti-oxide steel, and Fig. 1 (d) illustrates a HAZ structure in a steel of the present invention. In Fig. 1, reference numeral 1 stands for a weld metal, 2 for a weld heat-affected zone (HAZ), and 3 for a fusion line. In the HAZ structure, 4 stands for a  $\gamma$  grain boundary, GBF for a grain-boundary ferrite grain, FSP for a ferrite side-plate grain, IGF for an intragranular transformed ferrite grain, Bu for upper bainite, and MA for a martensite-austenite constituent.

#### Best Mode for Carrying Out the Invention

[0008] The present invention is explained hereunder in detail.

[0009] Figs. 1 (a) to (d) are illustrations schematically showing the concept of HAZ structure control. Fig. 1 (a) illustrates a HAZ structure in a conventional Ti-oxide steel, and Fig. 1 (d) illustrates a HAZ structure in a steel of the present invention. In Fig. 1, reference numeral 1 stands for a weld metal, 2 for a weld heat-affected zone (HAZ), and 3 for a fusion line. In the HAZ structure, 4 stands for a  $\gamma$  grain boundary, GBF for a grain-boundary ferrite grain, FSP for a ferrite side-plate grain, IGF for an intragranular transformed ferrite grain, Bu for upper bainite, and MA for a martensite-austenite constituent.

[0010] When the yield strength of a Ti-oxide steel is increased from the current 420 MPa class to the 500 MPa class, exceeding 460 MPa, and further to the 550 MPa class by adding alloy elements, a HAZ in close proximity to a fusion line becomes hard, thus making it difficult to secure a sufficient CTOD property. A HAZ structure in such a state is schematically shown in Fig. 1 (a). The primary cause to embrittle a HAZ is that coarse grain-boundary ferrite (GBF) grains and a ferrite side-plate (FSP) grains generated along the grain boundary of a coarse  $\gamma$  grain increase the susceptibility of the HAZ to brittle fracture with the increase in HAZ hardness, even though the interior of the coarse  $\gamma$  grain is fined by intragranular transformed ferrite (IGF) grains formed therein. Accordingly, it is necessary to decrease the susceptibility to brittle fracture by fining the GBF grains and FSP grains. The secondary cause of the embrittlement is that increased amounts of alloy elements added for strength enhancement increase the hardenability of the HAZ and a large number of microscopic brittle phases called MA (martensite-austenite constituent) are generated, which accelerate the occurrence of brittle fracture. Also, when a yield strength not lower than 460 MPa is to be achieved, it is necessary to decrease MA to the greatest possible extent. From what is described above, it is a guideline for achieving a satisfactory CTOD property of welded joints under a high yield strength to remove the two causes of embrittlement described above while maintaining the metallographic effect (IGF effect) of Ti-oxide steel. In other words, the gist of the present invention is to control a HAZ structure so as to satisfy the following three points at the same time:

- (1) To fine GBF grains and FSP grains generated along the boundaries of  $\gamma$  grains in a HAZ in close proximity to a fusion line.
- (2) To fine the interior of  $\gamma$  grains in a HAZ in close proximity to a fusion line by generating IGF grains therein.
- (3) To reduce the amount of MA produced in a HAZ in close proximity to a fusion line.

[0011] First, a means to achieve item (1) will be explained. In order to fine the coarse GBF grains and FSP grains, which are attributable to the occurrence of brittle fracture, it is necessary to make the  $\gamma$  grains smaller. With the aim of strongly suppressing the growth of the  $\gamma$  grains in the HAZ in close proximity to the fusion line heated higher than 1,400°C, an intensive study has been carried out on a wide variety of steel constituents. As a result, a technology has been invented in which a large number of ultrafine 0.01 to 0.1  $\mu\text{m}$  particles of oxide composed of Mg and Al are dispersed in the steel by appropriately controlling Mg and Al, and 0.01 to 0.5  $\mu\text{m}$  particles of TiN are precipitated in a

compounded form with the oxide particles used as nuclei. The TiN particles precipitated in the compounded form are thermally stable without growing or dissolving even in close proximity to the fusion line and therefore they can strongly pin  $\gamma$  grain boundaries to not allow their movement. Even if welding is carried out with a large amount of weld heat input, the size of the  $\gamma$  grains in close proximity to the fusion line can be kept on the order of 100  $\mu\text{m}$ . In some cases, these pinning particles existing on the  $\gamma$  grain boundaries directly function by themselves as transformation nuclei for the GBF grains and FSP grains, and therefore an increase of transformation places also contributes to the fining of the GBF grains and FSP grains. The existence of not less than 10,000 pieces/ $\text{mm}^2$  of such TiN particles precipitated in the compounded form fines the GBF grains and FSP grains to a size not adversely affecting a CTOD property. If the TiN particles precipitated in the compounded form are less than 10,000 pieces/ $\text{mm}^2$ , the fining of the  $\gamma$  grains and the number of transformation nuclei on the  $\gamma$  grain boundaries become insufficient, and consequently, the GBF grains and FSP grains are not sufficiently fined, thus deteriorating the CTOD property. In some cases, sulfide is precipitated in a compounded form on the TiN particles, but this does not adversely affect their above described functions as pinning particles or transformation nuclei.

**[0012]** Fig. 1 (b) is a schematic diagram showing a HAZ structure to which only the technique of the item (1) explained above is applied. Although the GBF grains and FSP grains are fined, the interior of the  $\gamma$  grains is covered by a brittle structure including MA, called upper bainite, and a sufficient CTOD property cannot be acquired by this technique only. Therefore, the technique of the item (2) explained hereunder must be jointly used.

**[0013]** A means to achieve the item (2) will be explained. According to the present invention, Mg is intentionally added in order to generate the above ultrafine oxide particles in large numbers. Since Mg is also contained in oxide particles of an ordinary size (several  $\mu\text{m}$ ), a study was made, in the process of the present invention, to generate IGF grains by utilizing such relatively large Mg-containing oxide particles. As a result, the following three conditions was found to be important for IGF transformation nuclei:

- ① At least, a minimum number of particles exist.
- ② The particles have an appropriate size.
- ③ The particles contain Mn.

**[0014]** From the viewpoint of the condition ①, it is necessary that at least not less than 10 pieces/ $\text{mm}^2$  of IGF transformation nuclei exist in a stable manner in a HAZ in close proximity to a fusion line. If the IGF transformation nuclei are less than 10 pieces/ $\text{mm}^2$ , the fining of the HAZ structure becomes insufficient.

**[0015]** From the viewpoint of the condition ②, it is necessary for particles to have a size not smaller than 0.5  $\mu\text{m}$  in order to effectively function as IGF transformation nuclei. If the size of the particles is smaller than 0.5  $\mu\text{m}$ , their ability as IGF transformation nuclei is considerably lowered. In order to satisfy this condition, it was studied, in the process of the present invention, to use oxide particles not smaller than 0.5  $\mu\text{m}$  as the IGF transformation nuclei. However, oxide particles exceeding 10  $\mu\text{m}$  are undesirable because they act as origins from which brittle fracture starts.

**[0016]** With respect to the viewpoint of the condition ③, it was found that particles need to contain not less than 0.3 wt% of Mn in order to effectively function as IGF transformation nuclei. For this purpose, it is desirable to incorporate Mn into the oxide particles of 0.5 to 10  $\mu\text{m}$ . Mg, Al and Ti are essential for the present invention in order to generate the ultrafine pinning particles, which consist of (Mg, Al) oxide and Ti nitride, explained in the item (1). Since these elements have deoxidizing power stronger than Mn has, the oxide particles of 0.5 to 10  $\mu\text{m}$  are mainly composed of Mg, Al and Ti. Therefore it is difficult to stably incorporate not less than 0.3 wt% of Mn into the oxide particles of 0.5 to 10  $\mu\text{m}$ . Because of this, it has been considered, in the process of the present invention, that Mn-containing sulfide is precipitated in a compounded form on the oxide particles. By using a means like this, Mn content in the compounded particles can be stably increased to 0.3 wt% or higher and the particles can effectively function as IGF transformation nuclei. A study was made to search for conditions for precipitating the Mn-containing sulfide in a compounded form on the oxide particles, and resultantly, Mg content in the oxide particles has proven to be important. In the event of oxide particles containing not less than 10 wt% of Mg, the Mn-containing sulfide was compounded with the oxide particles. On the other hand, in the event of oxide particles having an Mg content of less than 10 wt%, the sulfide was not compounded therewith but existed separately. To sum up, it was found that the Mn-containing sulfide was able to be stably compounded with, and precipitated on, the oxide particles of 0.5 to 10  $\mu\text{m}$  by incorporating not less than 10 wt% of Mg into the oxide particles. As a result of this, IGF transformation nuclei at not less than 10 pieces/ $\text{mm}^2$  of 0.5 to 10  $\mu\text{m}$  and containing not less than 0.3 wt% of Mn can be secured in the compounded form of the oxide and the sulfide. However, it should be noted that, if the total addition amount of Ca, REM, and Zr exceeds 0.02 wt%, Mn is no longer incorporated into the sulfide compounded with the oxide to cause Mn content in the compounded particles to fall below 0.3 wt%.

**[0017]** Fig. 1 (c) is a schematic diagram showing a HAZ structure to which the techniques of the items (1) and (2) explained above are jointly applied. The HAZ structure is fined by generating a large number of IGF grains in addition to the fining of GBF grains and FSP grains. If the amount of added alloy constituents is inappropriate, the amount of

MA generated is increased to deteriorate a CTOD property. Therefore, it is necessary to stably enhance the CTOD property by jointly using the technique of the item (3) explained below.

[0018] A means to achieve the item (3) will be explained. It is known that MA generating behavior in a HAZ greatly depends on its hardenability and cooling rate. In the present invention, the hardenability of a HAZ is greatly affected not only by the constituents of a steel but by the size of  $\gamma$  grains and the IGF generating ability thereof. In the case of a conventional steel, the size of  $\gamma$  grains and their IGF generating ability have hardly been taken into consideration with respect to the hardenability of a HAZ. On the other hand, a steel of the present invention, in which  $\gamma$  grains are smaller and besides IGF generating ability is higher to cause places of transformation to increase on  $\gamma$  grain boundaries and within  $\gamma$  grains, has a feature that the hardenability of a HAZ is remarkably lowered relative to a conventional steel having the same chemical compositions. With regard to the steel of the present invention having such feature, the effect of alloy contents on MA generation was intensively studied with the cooling rate (cooling time from 800°C to 500°C being about 15 sec) used in the execution of welding for offshore structures and the ranges of C and Mn of the present invention taken as preconditions. As a result, the following two points have become apparent:

- ④ An increase of the Nb content to a higher level than before can hardly increase the amount of MA generated in a HAZ.
- ⑤ There is a discontinuous but strong correlation between the total amount of Cu, Ni, Cr, and Mo, and the amount of MA in a HAZ.

[0019] From the viewpoint of the item ④, it has been found that, even if Nb content is increased to 0.05 wt%, its effect on the amount of MA generated in the HAZ is insignificant. To give examples of Nb actually used in a conventional steel plate (CTOD guaranteed steel for welded joints) for offshore structures, 0.02 wt% is the upper limit of Nb for a 420 MPa-class yield strength in the case of "Proceedings of 12th International Conference on OMAE, 1993, Glasgow, UK, ASME, Volume III-A, pp. 207 - 214," 0.021 wt% is the upper limit of Nb for a 460 MPa-class yield strength in the case of "Proceedings of 12th International Conference on OMAE, 1993, Glasgow, UK, ASME, Volume III-A, pp. 199 - 205," and Nb is 0.024 wt% for a 420 MPa-class yield strength in the case of "Proceedings of 12th International Conference on OMAE, 1994, Houston, ASME, Volume III, pp. 307 - 314." As described above, an Nb content on the order of 0.02 wt% has been substantially an upper limit. On the contrary, the present invention has the advantage of allowing Nb up to 0.05 wt% to be effectively used.

[0020] From the viewpoint of the item ⑤, it has been found that, when the total amount of Cu, Ni, Cr, and Mo exceeds 3.0 wt%, the amount of MA in a HAZ sharply increases. From the above findings, a guideline for composition designing is obtained that Nb is utilized as much as possible to increase the base metal strength of a thicker plate while reducing Cu, Ni, Cr, and Mo which accelerate MA generation, in cases where plate thickness is enlarged, for example, to the order of 76.2 mm while maintaining a yield strength not lower than 460 MPa, particularly of the 500 to 550 MPa class. Also, the reduction of Cu, Ni, Cr, and Mo is desirable in terms of alloy cost.

[0021] Fig. 1 (d) is a schematic diagram showing a HAZ structure to which the technique of the item (3) explained above and the techniques of the items (1) and (2) are jointly applied. The HAZ structure is sufficiently fined and besides the amount of MA is stably reduced and, therefore, a satisfactory CTOD property of welded joints is achieved for a higher strength. Thus, the present invention becomes feasible by implementing the techniques of items (1), (2) and (3) at the same time.

[0022] The reasons for restricting chemical constituents will be described. In the description of chemical constituents described below, % means weight %.

[0023] C at not less than 0.04 % is necessary in order to secure the strength and toughness of a base metal and a HAZ. However, if the C content exceeds 0.14 %, the toughness of the base metal and the HAZ is deteriorated and also the weldability is deteriorated, and therefore 0.14 % is the upper limit.

[0024] Si can be added for deoxidation. However, if the Si exceeds 0.4 %, HAZ toughness is deteriorated. In the present invention, Al, Ti, or Mg can also be used for deoxidation and, therefore, the Si content should be as little as possible from the viewpoint of HAZ toughness. Since Si accelerates MA generation in a HAZ, it is an undesirable element for the present invention.

[0025] Mn at not less than 1 % is necessary to secure the strength and toughness of a base metal and a HAZ. Also, Mn is important for forming a sulfide that constitutes IGF transformation nuclei. However, if the Mn content exceeds 2.0 %, the base metal and HAZ are embrittled and also the weldability is deteriorated, and therefore 2.0 % is the upper limit.

[0026] P is an impurity element for the present invention and has to be reduced below 0.02 % in order to secure the satisfactory quality of a base metal and a HAZ.

[0027] S is a necessary element for the present invention. S at not less than 0.001 % has to be secured in order to precipitate sulfide on oxide particles as IGF transformation nuclei in a compounded form. However, if the S content exceeds 0.005 %, the toughness of a base metal and a HAZ is deteriorated, and therefore 0.005 % is the upper limit.

[0028] Nb is extremely effective in enhancing the strength of a base metal while minimizing the deterioration of the toughness of a HAZ. Also, Nb is effective in enhancing toughness through the fining of the structure of a base metal. For example, Nb at not less than 0.005 % is essential in order to acquire satisfactory base metal toughness while achieving a yield strength of the 500 MPa class for a plate thickness of 76.2 mm. However, if the Nb content exceeds 0.05 %, the toughness of a HAZ is deteriorated by an increase in the amount of MA or by precipitation hardening, and therefore 0.05 % is the upper limit. Nb is an element that should be positively used for successfully manufacturing a base metal according to the present invention, and it is desirable to make effective use of Nb at not less than 0.02 %.

[0029] Al, together with Mg, forms ultrafine oxide particles of 0.01 to 0.1  $\mu\text{m}$  and functions as pinning particles in company with TiN precipitated in a compounded form on the oxide particles and further as transformation nuclei for GBF particles and FSP grains, thereby fining a HAZ structure. In order to achieve this, Al at not less than 0.001 % is necessary. If the Al is less than 0.001 %, it is impossible to secure the required number of ultrafine oxide particles for obtaining not less than 10,000 pieces/ $\text{mm}^2$  of compounded TiN particles, and therefore the fining of  $\gamma$  grains and the number of transformation nuclei on  $\gamma$  grain boundaries become insufficient. As a result, neither GBF grains nor FSP grains are sufficiently fined, thus deteriorating the HAZ toughness. However, if the Al exceeds 0.01 %, the Al content in the oxide constituting IGF transformation nuclei is increased and, as a counteraction to this, the Mg content in the oxide falls below 10 wt%. As a result, Mn-containing sulfide is hardly precipitated on the oxide particles to cause them to lose their ability as IGF transformation nuclei, and therefore it becomes difficult to secure not less than 10 pieces/ $\text{mm}^2$  of IGF transformation nuclei in a stable manner.

[0030] As described above, when the number of IGF transformation nuclei becomes insufficient, HAZ toughness is deteriorated. Accordingly, the upper limit of the Al is 0.01 %.

[0031] Ti forms TiN which precipitates on ultrafine (Mg, Al) oxide particles in a compounded form of 0.01 to 0.5  $\mu\text{m}$  in size and functions as pinning particles and further as transformation nuclei for GBF grains and FSP grains, thus fining a HAZ structure. For this purpose, Ti at not less than 0.005 % is necessary. If the Ti is less than 0.005 %, it is impossible to secure not less than 10,000 pieces/ $\text{mm}^2$  of TiN particles in the compounded form. As a result, neither GBF grains nor FSP grains are sufficiently fined, thus deteriorating the HAZ toughness. If both Si and Al are close to their lower limits, deoxidizing elements sometimes become insufficient, and therefore it is desirable to add Ti at not less than 0.01 % in order to cause Ti to take-over the deoxidation. However, if the Ti exceeds 0.03 %, TiC is precipitated or TiN particles are coarsened to a size as large as several  $\mu\text{m}$ , thereby embrittling a base metal and a HAZ. For the reasons stated above, the upper limit of the Ti is 0.03 %.

[0032] Mg plays the most important role in the present invention. The primary role of Mg is to form, together with Al, ultrafine oxide particles of 0.01 to 0.1  $\mu\text{m}$ , to function as pinning particles in company with TiN precipitated in a compounded form on the oxide particles and further to function as transformation nuclei for GBF grains and FSP grains, thereby fining HAZ structure. The secondary role of Mg is to accelerate the precipitation of Mn-containing sulfide in the compounded form on oxide particles of 0.5 to 10  $\mu\text{m}$  by being incorporated therein at 10 wt% or more to provide a function as transformation nuclei to the oxide particles, thereby fining the HAZ structure. In order to fulfill the two roles at the same time, Mg at not less than 0.0003 %, preferably at not less than 0.0005 %, is necessary. If the Mg is less than 0.0003 %, the contents of Si, Al, Ti, and the like in the oxide are increased and, as a counteraction to this, the Mg content in the oxide falls below 10 wt%. As a result, the Mn-containing sulfide is hardly precipitated on the oxide particles to cause them to lose their ability as IGF transformation nuclei, and therefore the number of IGF transformation nuclei becomes insufficient. At the same time, it becomes difficult to secure the required number of ultrafine (Mg, Al) oxide particles for obtaining not less than 10,000 pieces/ $\text{mm}^2$  of compounded TiN particles. However, if the Mg exceeds 0.005 %, its metallographic effect is saturated, and therefore this value is set as its upper limit.

[0033] O constitutes ultrafine (Mg, Al) oxide particles that have a HAZ pinning effect while it constitutes Mg-containing oxide particles of 0.5 to 10  $\mu\text{m}$  that function as IGF transformation nuclei in a HAZ. In order to fulfill these two roles, O at not less than 0.001 % is necessary. If the O is less than 0.001 %, it becomes difficult to secure the necessary number of ultrafine oxide particles for obtaining not less than 10,000 pieces/ $\text{mm}^2$  of compounded TiN particles and securing not less than 10 pieces/ $\text{mm}^2$  of oxide particles of 0.5 to 10  $\mu\text{m}$ . However, if the O exceeds 0.005 %, coarse oxide particles exceeding 10  $\mu\text{m}$  are generated in a large number and they act as origins from which brittle fracture starts in a base metal or a HAZ, and therefore 0.005 % is set as the upper limit.

[0034] N forms TiN which precipitates on ultrafine (Mg, Al) oxide particles in a compounded form of 0.01 to 0.5  $\mu\text{m}$  in size and functions as pinning particles and further as transformation nuclei for GBF grains and FSP grains, thereby fining the HAZ structure. For this purpose, N at not less than 0.001 % is necessary. If the N is less than 0.001 %, it is impossible to secure not less than 10,000 pieces/ $\text{mm}^2$  of TiN particles in the compounded form. However, if the N exceeds 0.01 %, solute N is increased to cause a base metal and a HAZ to be embrittled and surface properties of a cast slab to be deteriorated, and therefore this value is set as the upper limit.

[0035] The reasons to limit selective elements will be explained hereunder.

[0036] Ca, REM and Zr can be added as deoxidizing agents or desulfurizing agents. They contribute to the reduction of O content by acting as deoxidizing agents. As desulfurizing agents, they contribute to the reduction of S content

while they control the shape of sulfide. In order to improve the material quality of a base metal and a HAZ through these effects, the content of each element is required to be 0.0005 % or more. If these elements are too large in amount, they are mixed in IGF transformation nuclei to decrease the Mg content and Mn content in oxide and sulfide constituting the IGF transformation nuclei, and thus the IGF transformation nuclei lose their function. In this sense, the upper limits of Ca, REM and Zr are 0.005 %, 0.01 % and 0.01 %, respectively, and it is necessary to limit the total amount of the three elements to 0.02 % or less. REM here indicates lanthanoid elements such as La and Ce, and even if a misch metal made up of these elements mixed together is alternatively added, the effect described above can be obtained.

[0037] Cu, Ni, Cr and Mo can be utilized to enhance the strength, toughness, corrosion resistance and the like, of a base metal. For this purpose, any content of these elements has to be 0.05 % or more. Up to now, these elements have been positively used in cases where it is necessary to attain the enhancement of the strength and toughness of a base metal and the enlargement of plate thickness range at the same time. In the present invention, it is desirable to reduce these elements to the possible extent, from the viewpoint of securing the CTOD property of a HAZ. In this sense, the upper limits of Cu, Ni, Cr and Mo have to be controlled to 1.5 %, 3.0 %, 0.5 % and 0.5 %, respectively, and further, the total amount of these elements must be adjusted not to exceed 3.0 %. If any of these elements exceeds its upper limit or if the total amount of these elements exceeds 3.0 %, the CTOD property of a HAZ is remarkably deteriorated.

[0038] V effectively enhances the strength of a base metal and a HAZ by the precipitation strengthening. For this purpose, V at not less than 0.005 % is necessary. However, if the V content exceeds 0.05 %, weldability and HAZ toughness are deteriorated, and therefore, 0.05 % is set as the upper limit.

[0039] B is effective in enhancing the strength and toughness of a base metal. For this purpose, not less than 0.0001 % of B is necessary. However, if the B content exceeds 0.003 %, weldability is remarkably deteriorated, and therefore, 0.003 % is set as the upper limit.

[0040] A steel of the present invention undergoes the adjustment of chemical compositions to specified values and is continuously cast into a slab in a steelmaking process in the steel industry, and the slab is manufactured into a steel plate through processes of reheating, rolling, cooling, and heat-treatment, these being controlled in various ways. In order to obtain a yield strength of 460 MPa, preferably the 500 to 550 MPa class, for a thick plate having a thickness such as 76.2 mm, it is effective to use direct quenching or accelerated cooling after rolling in order to make the best possible use of Nb content. Further, strength and toughness can be adjusted by tempering. Also, it is possible to apply hot-charge rolling without cooling a cast slab once. The toughness of a HAZ is determined not only by chemical compositions but also by the state of the dispersion of pinning particles and that of IGF transformation nuclei. The state of the dispersion of these particles is not greatly changed in the course of manufacturing a base metal. Accordingly, the toughness of a HAZ does not greatly depend on the manufacturing processes of a base metal and therefore each of the reheating, rolling, and heat-treating processes can be of any type.

[0041] The state of the dispersion of inclusions specified in the present invention is quantitatively measured by methods such as those described below.

[0042] The number of TiN particles of 0.01 to 0.5  $\mu\text{m}$  including oxide composed of Mg and Al is determined by: preparing a sampling replica specimen taken from an arbitrary position of a base-metal steel plate, observing the specimen using a transmission electron microscope (TEM) under the magnification of 10,000 to 50,000 so as to cover an area of at least 1,000  $\mu\text{m}^2$ , measuring the number of TiN particles having sizes falling within the targeted range, and converting it into the number of particles per unit area (pieces/ $\text{mm}^2$ ). Here, the identification of (Mg, Al) oxide particles with TiN particles is performed by means of composition analysis using energy-dispersive X-ray spectroscopy (EDS) annexed to the TEM and crystalline structure analysis of electron diffraction images using the TEM. In the event that such identification is too intricate to be performed for all the kinds of compounded inclusions to be measured, the following simpler process is used. To begin with, square inclusions are regarded as TiN particles and the number of TiN particles each having an inclusion therein and a size falling within the targeted range is measured. Then, with respect to at least 10 particles among TiN particles precipitated in the compounded form, the number of which has been measured by this method, detailed identification is performed according to the procedures stated above to determine the proportion in which (Mg, Al) oxide is compounded with TiN. After that, the first measured number of TiN particles precipitated in the compounded form is multiplied by this proportion. If carbide particles in the steel hinder the above TEM observation, the observation of the targeted compounded inclusions can be made easier by aggregating and coarsening the carbide particles by heat treatment at 500°C or lower.

[0043] The number of particles of 0.5 to 10  $\mu\text{m}$  formed by compounding oxide with Mn-containing sulfide can be measured by a method such as that described below. To begin with, a polished specimen with a mirror finished surface is prepared by cutting a small piece of specimen out of an arbitrary position of a base-metal steel plate, the specimen is observed using an optical microscope under the magnification of 1,000 so as to cover an area of at least 3  $\text{mm}^2$ , the number of particles having sizes falling within the targeted range is measured, and the measured number is converted into the number of particles per unit area (pieces/ $\text{mm}^2$ ). Then, at least 10 randomly selected particles taken from the same specimen and having sizes falling within the targeted range undergo composition analysis using a

wavelength-dispersive X-ray spectroscope (WDS) annexed to the scanning electron microscope (SEM). Here, if Fe in the base steel is detected in the analyzed values of these particles, the Fe is removed from the analyzed values and then the composition of the particles is determined. Among the particles thus measured, particles in which O and S are detected at the same time and which include Mn at not less than 0.3 wt% are considered to be effective as IGF transformation nuclei, thereby determining the proportion of IGF transformation nuclei to the particles of 0.5 to 10  $\mu\text{m}$ . The number of particles first measured by the optical microscope is multiplied by this proportion. As a simpler method, element mapping is performed on the specimen stated above, thereby measuring the number of particles of 0.5 to 10  $\mu\text{m}$  in which three elements, O, S and Mn, coexist.

#### Example

**[0044]** Table 1 shows the chemical compositions of the continuous-cast steels, and Table 2 shows the thickness of each steel plate, the manufacturing method thereof, the number of pinning particles, the number of IGF transformation nuclei, the material quality of base metals, the welding conditions, and the toughness of each HAZ.

**[0045]** The steels of the present invention have plate thicknesses of 38.1 to 76.2 mm, base-metal yield strengths (YS) of 510 to 570 MPa, and satisfactory CTOD exceeding 0.2 mm at  $-10^{\circ}\text{C}$  in a multilayered joint bond part (CGHAZ) made by submerged arc welding with weld heat input of 3.5 to 10.0 kJ/mm.

**[0046]** On the other hand, comparative steels are inferior in base metal quality or HAZ quality for the plate thickness of 76.2 mm because of the inappropriate chemical composition. Steel 12 has an insufficient number of IGF transformation nuclei because the amount of S is too small, and is inferior in HAZ toughness. Steel 13 is inferior in base metal toughness and HAZ toughness because the amount of S is too large. Steel 14 is inferior in the strength and toughness of the base metal because the amount of Nb is too small. Steel 15 is inferior in HAZ toughness because the amount of Nb is too large. Steel 16 has an insufficient number of pinning particles because the amount of Al is too small, and is inferior in HAZ toughness. Steel 17 has an insufficient number of IGF transformation nuclei because the amount of Al is too large, and is inferior in HAZ toughness. Steel 18 has an insufficient number of pinning particles because the amount of Ti is too small, and is inferior in HAZ toughness. Steel 19 is inferior in base metal toughness and HAZ toughness because the amount of Ti is too large. Steel 20 and Steel 21 are insufficient in the number of pinning particles and in the number of IGF transformation nuclei because of too small amounts of Mg and O, respectively, and are inferior in HAZ toughness. Steel 22 has an insufficient number of pinning particles because the amount of N is too small, and is inferior in HAZ toughness. Steel 23 is inferior in HAZ toughness because the total amount of Cu, Ni, Cr and Mo is too large. Steel 24 has an insufficient number of IGF transformation nuclei because the total amount of Ca, REM and Zr is too large, and is inferior in HAZ toughness.



Table 1

Category	Steel	C	Si	Mn	P	S	Nb	Al	Ti	Mg	O	N	Others	Ca + REM + Zr	Cu + Ni + Cr + Mo
Invented steel	1	0.10	0.03	1.48	0.006	0.003	0.02	0.002	0.025	0.002	0.004	0.008	Ni: 0.4, Cu: 0.4, Mo: 0.1	0	0.9
	2	0.08	0.02	1.53	0.003	0.002	0.03	0.003	0.017	0.0003	0.004	0.002	Ni: 0.5, Cu: 0.5, V: 0.01	0	1.0
	3	0.05	0.08	1.55	0.003	0.003	0.03	0.003	0.015	0.003	0.002	0.003	Ni: 0.7, Cu: 0.6	0	1.3
	4	0.09	0.06	1.55	0.003	0.003	0.04	0.002	0.016	0.002	0.003	0.002	Ni: 0.6, Cu: 0.6	0	1.2
	5	0.08	0.09	1.88	0.004	0.002	0.03	0.003	0.010	0.003	0.002	0.003	Ni: 1.0, Cu: 0.6	0	1.6
	6	0.10	0.08	1.57	0.015	0.002	0.02	0.003	0.009	0.002	0.004	0.004	Ni: 0.4, Cr: 0.4, Ca: 0.0007	0.0007	0.8
	7	0.10	0.20	1.59	0.004	0.001	0.02	0.005	0.009	0.002	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	8	0.11	0.25	1.60	0.005	0.004	0.04	0.006	0.008	0.004	0.001	0.004		0	0
	9	0.11	0.25	1.60	0.005	0.004	0.04	0.008	0.008	0.004	0.001	0.004	Ca: 0.002, Zr: 0.001	0.003	0
	10	0.13	0.25	1.10	0.005	0.004	0.04	0.006	0.006	0.0004	0.001	0.004	REM: 0.004, B: 0.001	0.004	0
Comparative steel	11	0.13	0.25	1.10	0.005	0.004	0.04	0.006	0.006	0.004	0.001	0.004	REM: 0.004	0.004	0
	12	0.10	0.20	1.59	0.004	0.0008	0.02	0.005	0.009	0.002	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	13	0.10	0.20	1.59	0.004	0.006	0.02	0.005	0.009	0.002	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	14	0.10	0.20	1.59	0.004	0.001	0.003	0.005	0.009	0.002	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	15	0.10	0.20	1.59	0.004	0.001	0.06	0.005	0.009	0.002	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	16	0.10	0.20	1.59	0.004	0.001	0.02	0.008	0.009	0.002	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	17	0.10	0.20	1.59	0.004	0.001	0.02	0.012	0.009	0.002	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	18	0.10	0.20	1.59	0.004	0.001	0.02	0.005	0.003	0.002	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	19	0.10	0.20	1.59	0.004	0.001	0.02	0.005	0.003	0.002	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	20	0.10	0.20	1.59	0.004	0.001	0.02	0.005	0.003	0.002	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	21	0.10	0.20	1.59	0.004	0.001	0.02	0.005	0.009	0.0001	0.003	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	22	0.10	0.20	1.59	0.004	0.001	0.02	0.005	0.009	0.002	0.0007	0.005	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	23	0.10	0.20	1.59	0.004	0.001	0.02	0.005	0.009	0.002	0.003	0.0007	Ni: 0.6, Cu: 0.6, Ca: 0.002	0.002	1.2
	24	0.10	0.20	1.59	0.004	0.001	0.02	0.005	0.009	0.002	0.003	0.005	Ni: 2.0, Cu: 0.8, Mo: 0.3	0	3.1
													Ca: 0.02, REM: 0.01, Zr: 0.01	0.022	0

Chemical analysis is used to analyze Mg.

Table 2

Category	Steel	Plate Thickness (mm)	Manufacturing method of plate <sup>1)</sup>	Number of pinning particles <sup>2)</sup> (pcs/mm <sup>2</sup> )	Number of IGF transformation nuclei (pcs/mm <sup>2</sup> )	Base metal quality <sup>4)</sup>			Welding condition <sup>5)</sup> Weld heat input (kJ/mm)	CTOD of CGHAZ <sup>6)</sup>	
						YS (MPa)	TS (MPa)	RAZ (%)	VTrs (°C)	CTOD at -10°C (mm)	CTOD at -30°C (mm)
Invented steel	1	76.2	DQ-T	30000	30	550	610	60	-75	10.0	0.9
	2	76.2	DQ-T	20000	30	560	640	65	-80	3.5	0.8
	3	38.1	DQ-T	40000	20	510	570	70	-80	5.0	1.0
	4	76.2	DQ-T	40000	25	560	630	60	-90	3.5	0.9
	5	76.2	DQ-T	50000	20	570	680	65	-70	4.5	0.7
	6	76.2	ACC	100000	40	530	650	60	-70	3.5	0.8
	7	50.8	ACC	80000	30	530	670	60	-70	3.5	0.8
	8	76.2	DQ-T	15000	15	520	600	65	-80	3.5	0.8
	9	76.2	DQ-T	20000	20	520	590	60	-60	3.5	1.1
	10	76.2	ACC	15000	15	510	580	65	-60	3.5	0.9
	11	76.2	ACC	15000	15	510	580	65	-60	3.5	0.9
Comparative steel	12	76.2	ACC	80000	8	530	670	60	-70	3.5	0.15
	13	76.2	ACC	80000	30	530	670	40	-40	3.5	0.15
	14	76.2	ACC	80000	30	450	580	60	-40	3.5	0.15
	15	76.2	ACC	80000	30	560	680	50	-60	3.5	0.9
	16	76.2	ACC	7000	30	530	670	60	-70	3.5	0.1
	17	76.2	ACC	90000	7	530	670	60	-70	3.5	0.1
	18	76.2	ACC	8000	30	520	670	60	-60	3.5	0.1
	19	76.2	ACC	80000	30	550	680	50	-30	3.5	0.07
	20	76.2	ACC	6000	6	530	670	60	-70	3.5	0.1
	21	76.2	ACC	7000	7	530	670	60	-70	3.5	0.05
	22	76.2	ACC	7000	30	520	670	60	-60	3.5	0.13
	23	76.2	ACC	80000	30	580	720	50	-50	3.5	0.02
	24	76.2	ACC	80000	5	530	670	65	-60	3.5	0.05

- 1) DQ: Direct quenching, ACC: Accelerated cooling, T: Tempering, CR: Controlled rolling
- 2) TiN particles of 0.01 to 0.5  $\mu\text{m}$  including oxide composed of Mg and Al
- 3) Particles of 0.5 to 10  $\mu\text{m}$  containing Mn not less than 0.3 wt% in the compounded form of oxide and sulfide
- 4) YS, TS, and VTrs are tested at the center position of plate thickness; RAZ is a mean value of 3 specimens
- 5) Multilayered welding by submerged arc welding, V groove
- 6) Compliant with BS7448, without PWH, the lowest value of 3 specimens shown, CGHAZ being abbreviation for Coarse Grain HAZ, a fatigue notch cut in on a fusion line on the I groove side

## Industrial Applicability

[0047] The present invention remarkably improves the CTOD property of welded joints of a high-strength, ultra-heavy steel plate, and as a result, it paves the way for a weight reduction and upsizing of offshore structures. This allows the construction cost of offshore structures to be sharply reduced and energy development in much deeper seas area to be carried out.

## Claims

1. A steel plate having an excellent CTOD property in a weld heat-affected zone and a yield strength not lower than 460 Mpa, **characterized by:**  
having a chemical composition comprising, in terms of wt%,

C: 0.04 to 0.14 %,  
Si: 0.4 % or less,  
Mn: 1.0 to 2.0 %,  
P: 0.02 % or less,  
S: 0.001 to 0.005 %,  
Al: 0.001 to 0.01 %,  
Ti: 0.005 to 0.03 %,  
Nb: 0.005 to 0.05 %,  
Mg: 0.0003 to 0.005 %,  
O: 0.001 to 0.005 %, and  
N: 0.001 to 0.01 %;

with the balance consisting of iron and unavoidable impurities: and

having TiN particles of 0.01 to 0.5  $\mu\text{m}$  at not less than 10,000 pieces/ $\text{mm}^2$ , containing oxides composed of Mg and Al, and particles of 0.5 to 10  $\mu\text{m}$  at not less than 10 pieces/ $\text{mm}^2$ , containing not less than 0.3 wt% of Mn in the compounded form of oxide and sulfide.

2. A steel plate having an excellent CTOD property in a weld heat-affected zone and a yield strength not lower than 460 Mpa according to claim 1, **characterized by:**  
having a chemical composition further comprising, in terms of wt%, one or more of

Ca: 0.0005 to 0.005 %,  
REM: 0.0005 to 0.01 %, and  
Zr: 0.0005 to 0.01 %,

wherein the total amount of Ca, REM and Zr is not more than 0.02 %.

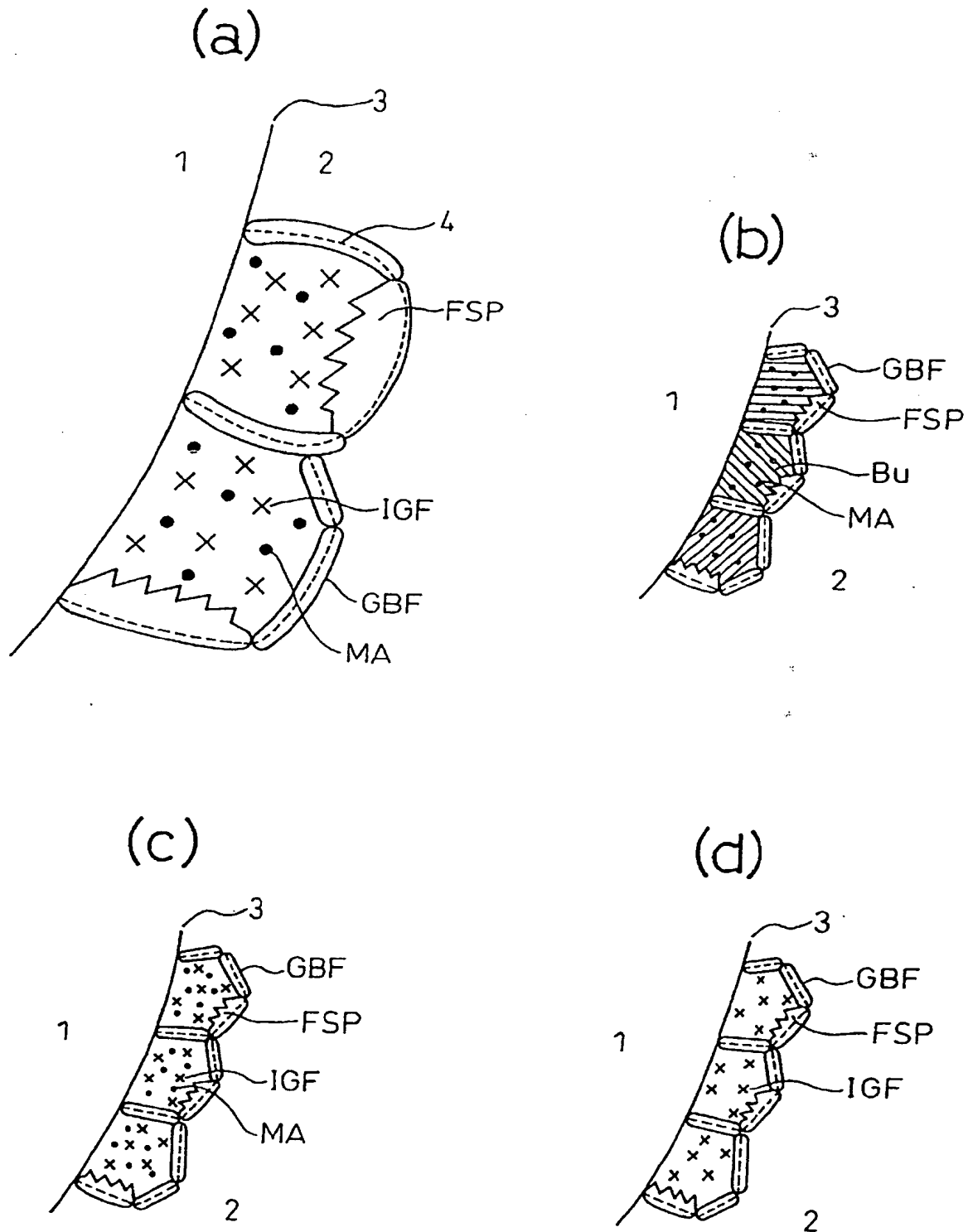
3. A steel plate having an excellent CTOD property in a weld heat-affected zone and a yield strength not lower than 460 Mpa according to claim 1 or 2, **characterized by:**

having a chemical composition further comprising, in terms of wt%, one or more of

Cu: 0.05 to 1.5 %,  
Ni: 0.05 to 3.0 %,  
Cr: 0.05 to 0.5 %,  
Mo: 0.05 to 0.5 %,  
V: 0.005 to 0.05 %, and  
B: 0.0001 to 0.003 %,

wherein the total amount of Cu, Ni, Cr and Mo is not more than 3.0 %.

Fig.1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/03876

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. <sup>7</sup> C22C38/00, 38/14, 38/58		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl. <sup>7</sup> C22C38/00, 38/14, 38/58		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 11-279684, A (Nippon Steel Corporation), 12 October, 1999 (12.10.99) (Family: none)	1-3
Y	JP, 11-293382, A (Nippon Steel Corporation), 26 October, 1999 (26.10.99) (Family: none)	1-3
Y	JP, 11-264048, A (Nippon Steel Corporation), 28 September, 1999 (28.09.99) (Family: none)	1-3
Y	JP, 10-298708, A (Nippon Steel Corporation), 10 November, 1998 (10.11.98) (Family: none)	1-3
Y	JP, 9-310147, A (Nippon Steel Corporation), 02 December, 1997 (02.12.97) (Family: none)	1-3
Y	JP, 9-157787, A (Nippon Steel Corporation), 17 June, 1997 (17.06.97) (Family: none)	1-3
Y	JP, 7-278736, A (Sumitomo Metal Industries, Ltd.), 24 October, 1995 (24.10.95) (Family: none)	1-3
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 25 May, 2001 (25.05.01)		Date of mailing of the international search report 05 June, 2001 (05.06.01)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/03876

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages.	Relevant to claim No.
A	JP, 10-265890, A (Nippon Steel Corporation), 06 October, 1998 (06.10.98) (Family: none)	1-3
A	JP, 10-265897, A (Nippon Steel Corporation), 06 October, 1998 (06.10.98) (Family: none)	1-3
A	JP, 11-236645, A (Nippon Steel Corporation), 31 August, 1999 (31.08.99) (Family: none)	1-3
A	JP, 11-286743, A (Nippon Steel Corporation), 19 October, 1999 (19.10.99) (Family: none)	1-3
A	JP, 9-176730, A (Sumitomo Metal Industries, Ltd.), 08 July, 1997 (08.07.97) (Family: none)	1-3
A	JP, 10-8132, A (Sumitomo Metal Industries, Ltd.), 13 January, 1998 (13.01.98) (Family: none)	1-3
A	JP, 11-293383, A (Nippon Steel Corporation), 26 October, 1999 (26.10.99) (Family: none)	1-3
A	JP, 10-265896, A (Nippon Steel Corporation), 06 October, 1998 (06.10.98) (Family: none)	1-3
A	JP, 10-53838, A (Nippon Steel Corporation), 24 February, 1998 (24.02.98) (Family: none)	1-3
A	JP, 10-1744, A (Nippon Steel Corporation), 06 January, 1998 (06.01.98) (Family: none)	1-3

Form PCT/ISA/210 (continuation of second sheet) (July 1992)